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(54) Title: MODIFIED FIBROUS PRODUCTS AND METHOD FOR THEIR MANUFACTURE

(57) Abstract

The modified fibrous products, especially fabrics, nonwovens, knitwears, leathers and the like, comprise chitosan after treatment by chitosan as a modifying material. The chitosan is microcrystalline chitosan and the product contains microcrystalline chitosan particles bonded to adjacent particles and the structure of the fibrous product mainly by hydrogen bonds. In a method of manufacture of the modified products, the microcrystalline chitosan gel-like dispersion is brought in contact with the products, whereafter the products are dried.

MODIFIED FIBROUS PRODUCTS AND METHOD FOR THEIR MANUFACTURE

The invention relates to modified fibrous products and method for their manufacture.

Up to now the standard chitosan poly(2-deoxy-2-amino-glucose) has been used in several applications especially in the textile industry for the modification of fibrous products. The standard chitosan has been applied for coated textiles as a water repellent agent, for nonwoven fabrics and paper as a preparate improving wet and dry strength and also as a bonding agent and for textiles as a agent improving dyeability especially in the case of printing.

The standard chitosan was used also for textiles made from wool fibres to improve their shrinkage and for textiles of synthethic fibres as an antistatic agent. The standard chitosan was applied together with chlorophospharenes to produce the flame resistant textiles and plastics.

The well-known textiles modified by chitosan and methods for their manufacture require the use of standard chitosan dissolved in the aqueous acidic solution. The products obtained on a base of the chitosan salts are characterized by non-durability against water.

The manufacture of water durable products impregnated by chitosan according to the well-known methods is concerned with regeneration of chitosan salts by using queous alkaline solutions as an additional treatment.

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The well-known methods need several stages to obtain water durable products. The products obtained at the same time change the specific properties under the additional treatments.

The well-known textiles containing chitosan as well as the methods for their manufacture are described among others in R.A.A. Muzzarelli's monography "Chitin", Pergamon Press, New York, 1977, Chemical Week, v. 135(12), p. 40, 1984, Technik Wlokiennik, v. 32(4), p. 105-106, 1983, Wlokna Chemiczne, v. 8(1), p. 65-82, 1982, Journal of Society of Dyer Colourist, v. 100(10), p. 298-303, 1984, Leather Science, v. 22(8), p. 244, 1975 as well as in US Patent No. 2 047 218, Japan Patents No 70/02799; 79/93200; 84/180460; 70/02799; 83/40545; 84/216814; 82/82576 and Polish Patent No. 127 951.

From Polish Patent 125 995 there is known a microcrystalline chitosan production method based on the aggregation system. The product obtained according to this method has been formed in a form of gel-like dispersion or powder. Microcrystalline chitosan showed a water retention value (WRV) in a powder form within a range of 200-500%, in a gel-like dispersion 500-2000% adequately, the average molecular weight of 10^4-10^6 as well as a deacetylation degree not less than 30%.

The microcrystalline polymers are defined by C. A. Battista in O. A. Battista: "Microcrystalline Polymers Science", McGraw Holl Publ., New York, 1975.

The microcrystalline chitosan has got the same chemical structure as standard chitosan raw material. However, it differs from this raw material by super-molecular structure.

The object of this invention is to produce modified fibrous products containing chitosan by means of microcrystalline chitosan, especially a gel-like dispersion, using for example spraying or foularding in different forms.

According to the present invention there is provided modified fibrous products, especially fabrics, nonwovens, knitwears, leathers and the like, comprising chitosan after treatment by chitosan in a microcrystalline form, the product containing microcrystalline chitosan particles bonded to adjacent particles and the structure of the fibrous product mainly by hydrogen bonds.

According to a preferred embodiment of the invention, the product contains not less than 0.01 wt.% of microcrystalline chitosan, preferably 0.5-10 wt.%.

According to a preferred embodiment of the invention, the product contains also modifying chemical additives up to 10 wt.% on the microcrystalline chitosan weight.

According to a preferred embodiment of the invention, the microcrystalline chitosan used as a modifying material for the modified fibrous products manufacture such as a gel-like dispersion preferably in water, has especially a water retention value of

the gel-like form within a range 500-2000% and 200-800% in the powder form, average molecular weight within a range 10^4-10^6, deacetylation degree not less than 30%, preferable 40-80% and preferably particle dimension within a range of 0.01 to 100 µm.

In accordance with a preferred embodiment of the method for manufacture of fibrous products of the invention, the microcrystalline chitosan gel-like dispersion, especially in water is brought in contact with the fibrous products, especially fabrics, nonwovens, knitwears, leathers and the like, preferably by dipping, immersing, spraying or foularding, whereafter the products are dried.

According to a preferred embodiment of the above-mentioned method, the microcrystalline gel-like dispersion used contains not less than 0.001 wt.% of the polymer on a dry weight and has a pH not less than 7.00, especially in a range 7.00-10.00.

Further, in accordance with a preferred embodiment of the method, the addition of the modifying chemical additives is carried out directly to the microcrystalline chitosan before or during distribution of microcrystalline particles into a liquid medium or to the liquid medium as well as during the modification of fibrous products, preferably by spraying through nozzles or similar.

The modified fibrous products as fabrics, nonwovens, knitwears or leather according to the invention are produced on a base microcrystalline chitosan. Microcrystalline chitosan forms the small aggregates in a dispersion, especially in a water, with average dimension within a range of 0.01-100 µm.

Figure 2 shows the scanning electron microscope photographs of the nonwoven modified by the microcrystalline chitosan (Fig. 2a, -x200/600) and the nonwoven fibres covered by the microcrystalline chitosan film (Fig. 2b, c, x1000) as well as the standard non-bonded nonwoven used as raw material (Fig. 2d, x200/600) and standard nonwoven bonded by acrylic resin (Fig. 2e, x200/600).

Figure 3 shows the scanning electron microscope photographs of the cotton fabric modified by microcrystalline chitosan (Fig. 3a, x200/600) as well as the individual cotton fibres of fabric (Fig. 3b, x1800). Figure 3c (x200/600) shows the standard cotton fabric for comparison.

Figure 4 shows the scanning electron microscope photographs of the cotton knitwear modified by microcrystalline chitosan (Fig. 4a, x200/600) as well as non-modified raw material (Fig. 4b, x200/600).

The modification of the fibrous products in accordance to the invention allows to obtain the microcrystalline chitosan products, especially films formed directly on the surface of fibrous products as fabrics, nonwovens, knitwears or leathers as well as into their porous structure. The thickness of microcrystalline chitosan film layer formed on the fibrous products is dependent among others to amount of microcrystalline chitosan used, type of method applied or system of drying.

The microcrystalline chitosan film is produced by formation of the powerful hydrogen bonds between microcrystalline particles, especially gel-like

Application of the microcrystalline chitosan gel-like dispersion for the fibrous products allows to cover their surface as well as to introduce to their porous system to form especially polymeric film, It can be possible to compress the individual aggregates of microcrystalline chitosan by a drying method for example to produce the modified fibrous produts.

The microcrystalline chitosan dispersion contains preferable 0.01-10 wt.% of polymer according to possibilities for covering the modified fibrous products characterized by optimal mechanical and super-molecular properties.

The well-known modified textiles containing standard chitosan are formed according to preparation of the chitosan acetate covered impregnated textiles, and eventually regeneration of chitosan in the aqueous alkaline solutions as well as subsequent purification of products obtained and drying. Therefore the well-known modified textiles need for preparation minimum 1-2 hours, whereas the modified fibrous products according to the invention can be prepared using a microcrystalline chitosan dispersion already after 1 minute. No more operations excluding drying is need for production of the fibrous products modified by microcrystalline chitosan.

For illustrating the invention, figures are enclosed, which show the raw material and the fibrous product.

Figure 1 shows the photographs of the microcrystalline chitosan gel-like dispersion made by optical microscope (Fig. 1a, Magnification 400) and by scanning electron microscope (Fig. 1b, magnification 1000).

aggregates. At the same time the suitable powerful hydrogen bonds are formed between microcrystalline chitosan and the covered fibrous products. The energy of these type of hydrogen bonds is connected mainly with type of fibrous material and conditions applied.

The properties of microcrystalline chitosan used for modification of the fibrous products effect directly on the modified products obtained. The main invention of the fibrous products modification as well as the method of their manufacture is the utilization of possibilities for the formation of hydrogen bonds between microcrystalline chitosan aggregates as well as microcrystalline chitosan and covered materials.

Another important object is to eventually apply chemical additives to the microcrystalline chitosan for modifying the structure and properties of products obtained. The modificators applied in the invention allow to moderate the possibilities for the suitable hydrogen bonds formation. The modificators create also suitable higher energetic hydrogen bonds reducing at the same time possibilities to connexion of the individual particles of microcrystalline chitosan.

Use of a wetting agent in the invention as example of modificators in a case of the modified nonwoven made of polyester fibres using the spraying system of microcrystalline chitosan dispersion containing 0.5 wt.% of polymer and 0.1 wt.% of lithium chloride on the dry weight of polymer causes to obtain the product characterized by a change of properties, in comparison with microcrystalline chitosan-nonwoven not modified with LiCl, for example tensile strength reduced for 1.12 times.

The important object of the invention is also to use a different reaction of the microcrystalline chitosan gel-like dispersion for manufacture of modified fibrous products. The specific porperties of microcrystalline chitosan is connected with Z-potential influence on the properties of the modified fibrous products.

Increase of pH of the microcrystalline chitosan reaction dispersion in the invention causes suitable changes of the modified fibrous products properties. For example augmentation of pH from 8.0 to 9,5 in a case of the microcrystalline chitosan dispersion used for modification of nonwovens causes to obtain the product characterized by a reduction of tensile strangth within a range of 8-15%.

The modified fibrous products obtained according to the invention covered by the microcrystalline chitosan, especially in a form of film, contain water insoluble modifying chitosan also in every stage of the formation process as well as contain through the whole formation time chitosan in the free amino form.

Certain advantages are achieved in a case of the modified fibrous products according to the invention. The microcrystalline chitosan material, especially films, formed on the surface of modified fibrous products or into their porous structure improves their mechanical properties such as for example tensile strength, acts as a bonding agent for nonwoven both combining the fibres as well as improving the mechanical properties. At the same time other properties of the modified fibrous products are improved by application of microcrystalline chitosan

At the same time the method in accordance with the invention is uncommonly simple and easy for practical realization, in comparison to well-known methods, giving the valuable products directly first of all by application of microcrystalline chitosan dispersion without any special additional finishing process.

Additional advantages of the invented method is to produce the modified fibrous products covered by the microcrystalline chitosan with special properties as for example purifity or sterilizity.

The object is further to defelop the modified fibrous products containing microcrystalline chitosan that can be used in a wide range of products as textiles, paper leather etc.

The following methods of the determination of properties of the modified fibrous products as well as chitosan have been applied:

- tensile strength and break elongation : SFS2983
- square mass : SFS3192
- tensile strength and elongation of the leather : SLP5

- electric conductivity and resistance : SFS5155
- LOI value : according to ASTM standard of 2863-70 (FTA Flammabilitys unit $\%O_2$)

as for example better dyability, ability for printing, shrinkage reduction, water repellency and flame resistancy or bacteriostatic action.

For example, in the cotton fabric modified by a microcrystalline chitosan dispersion, tensile strength was increased minimum by 10-15% and elongation by 25% in comparison with unmodified fabric.

In the nonwovens bonded by the microcrystalline chitosan dispersion according to the invention, tensile strength was increased minimum by 100-500% in comparison to raw materials. The amount of the microcrystalline chitosan applied in a case of nonwoven is minimum 15 times lower than in a case of the standard bonding agents, such as acrylic resins. At the same time, suitable better mechanical properties in a case of the invented modified nonwovens in comparison to well-known bonded nonwovens are obtained.

In the invention, the use of 4.3 wt.% of the microcrystalline chitosan on a dry weight of polymer in a case of nonwoven made of polyester fibres allows to obtain by a spraying method a modified product with a tensile strength of 37.3 cN/50 mm and elongation of 2%. At the same time this same nonwoven bonded by the standard acrylic bonding agent in amount of 33 wt.% on the dry weight of polymer is characterized by tensile strength of 34.8 cN/50 mm and elongation of 16%.

- deacetylation degree of chitosan :
  according to the infrared method described in the International Journal of Biological Macromolecules, v. 2, p. 115, 1980;

- water retention value of chitosan :
  according to the method described in the Cellulose Chemistry and Technology, v. 11, p. 633, 1977

- average molecular weight of chitosan :
  according to the method described in "Chitin", Pergamon Press, New York, 1977

The ingredients used were:

1. Microcrystalline chitosan gel-like dispersion according to Polish Patent 125 995 was obtained. Microcrystalline chitosan dispersion was prepared on a base of non-degraded and degraded chitosan.
2. Lithium chloride acts as an inorganic example of the structure moderator.
3. Sandozin NIT is a trade name of wetting agent. The function of this substance in the invented modified fibrous products is to moderate the structure of microcrystalline chitosan materials, especially films, as an example of organic moderating compound.
4. R-N1809 is a trade name of standard acrylic resin containing 45 wt.% on polymer. The function of this substance in the nonwoven is to bond the fibres together.

The invention is explained further in the following examples which do not restrict the scope of claims.

EXAMPLE 1

3.23 weight parts of the nonwoven made of polyester fibres characterized by specific weight of 26 g/m² and tensile strength for the standard conditions of 24.3 N/50 mm as well as in wet conditions of 0 N/50 mm and elongation in standard conditions of 1.0% as well as LOI of 17% was introduced to spraying using 0.5 wt.% dispersion of microcrystalline chitosan in water of pH 8,5 prepared from the microcrystalline chitosan gel-like raw material containing 2.25 wt.% of polymer characterized by deacetylation degree of 62.5%, average molecular weight of 4.28×10^5 and water retention value WRVg of 770%. The wetness of sample was 412 wt.%. Then the product was dried at 40°C for 30 minutes.

The 3.39 weight parts of the modified nonwoven sample containing 4.95 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 34.7 N/50 mm and elongation of 2% as well as LOI of 17.6%.

At the same time the standard acrylic bonding agent of RN-1809 was used by this same method. The acrylic resin content in a nonwoven sample was 33 wt.% on a sample weight. The sample was characterized by tensile strength of 34.8 N/50 mm, elongation of 16% and LOI of 16.7%.

EXAMPLE 2

3.23 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 1 was introduced to spraying using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 1. The wetness of sample was 412 wt.%. Then the product was dried at 105°C for 5 minutes.

The 3.39 weight parts of the modified nonwoven sample containing 4.95 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 35,7 N/50 mm, elongation of 2% and LOI of 17,7%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 3

3.37 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 1 was introduced to spraying using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 1. The wetness of sample was 384 wt.%. Then the product was dried at 40°C for 30 minutes.

The 3.49 weight parts of the modified nonwoven sample containing 3.56 wt.% of microcrystalline chitosan was

obtained. The sample was characterized by tensile strength of 28.3 N/50 mm, elongation of 2% and LOI of 17,6%.

A sample, where the well-known acrylic resin used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 4

3.40 weight parts of the nonwoven made of polyester fibres characterized by specific weight of 26 g/m² and tensile strength for the standard conditions of 24.3 N/50 mm as well as in wet conditions of 0 N/50 mm and elongation in standard conditions of 1.0% as well as LOI of 17% was introduced to spraying using 0.5 wt.% dispersion of microcrystalline chitosan in water of pH 9,5 prepared from the microcrystalline chitosan gel-like raw material containing 2.25 wt.% of polymer characterized by deacetylation degree of 62.5%, average molecular weight of 4.28×10^5 and water retention value WRVg of 770%. The wetness of sample was 397 wt.%. Then the product was dried at 40°C for 30 minutes.

The 3.48 weight parts of the modified nonwoven sample containing 2.4 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 32 N/50 mm, elongation of 2% as well as LOI of 17.1%.

At the same time the standard acrylic bonding agent of RN-1809 was used by this same method. The acrylic resin content in a nonwoven sample was 33 wt.% on a sample weight. The sample was characterized by tensile strength of 34.8 N/50 mm, elongation of 16% and LOI of 16.7%.

EXAMPLE 5

3.40 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 4 was introduced to spraying using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 1. The wetness of sample was 397 wt.%. Then the product was dried at 105°C for 30 minutes.

The 3.48 weight parts of the modified nonwoven sample containing 2.4 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 29.5 N/50 mm, elongation of 2% and LOI of 17,2%. As wet, after soaking 10 min in water, the sample was characterized by tensile strength of 8.7 N/50 mm and elongation of 1.5%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 6

3.27 weight parts of the nonwoven made of polyester fibres characterized by specific weight of 26 g/m² and tensile strength in the standard conditions of 24.3 N/50 mm as well as in wet conditions of 0 N/50 mm, elongation in standard conditions of 1.0% as well as LOI of 17% was introduced to spraying using 0.5 wt.% dispersion of microcrystalline chitosan in water of pH 9.7 prepared from the microcrystalline chitosan gel-like raw material containing 2.25 wt.% of polymer characterized by deacetylation degree of 62.5%, average molecular weight of 4.28×10^5 and water retention value WRVg of 770%. The wetness of sample was 408 wt.%. Then the product was dried at 40°C for 30 minutes.

The 3.36 weight parts of the modified nonwoven sample containing 2.8 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 32.6 N/50 mm.

At the same time the standard acrylic bonding agent of RN-1809 was used by this same method. The acrylic resin content in a nonwoven sample was 33 wt.% on a sample weight. The sample was characterized by tensile strength of 34.8 N/50 mm, elongation of 16% and LOI of 16.7%.

EXAMPLE 7

3.43 weight parts of the nonwoven made of polyester fibres characterized by specific weight of 26 g/m² and tensile strength in the standard conditions of

24.3 N/50 mm as well as in wet conditions of 0 N/50 mm, elongation in standard conditions of 1.0% as well as LOI of 17% was introduced to spraying using 0.5 wt.% dispersion of microcrystalline chitosan in water of pH 7.6 prepared from the microcrystalline chitosan gel-like raw material containing 2.25 wt.% of polymer characterized by deacetylation degree of 62.5%, average molecular weight of 4.28×10^5 and water retention value WRVg of 770%. The wetness of sample was 300 wt.%. Then the product was dried at 105°C for 5 minutes.

The 3.52 weight parts of the modified nonwoven sample containing 2.6 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 22.1 N/50 mm and elongation of 2%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 8

3.45 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 7 was introduced to spraying using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 1. The wettness of sample was 668 wt.%. Then the product was dried at 105°C for 5 minutes.

EXAMPLE 10

3.28 weight parts of the nonwoven made of polyester fibres characterized by specific weight of 27 g/m² and tensile strength in the standard conditions of 6.2 N/50 mm as well as in wet conditions of 0 N/50 mm and elongation in standard conditions of 1.0% as well as LOI of 17.0% was introduced to spraying using 0.5 wt.% dispersion of microcrystalline chitosan in water of pH 7.6 prepared from the microcrystalline chitosan gel-like raw material containing 2.25 wt.% of polymer characterized by deacetylation degree of 62.5%, average molecular weight of 4.28×10^5 and water retention value WRVg of 770%. The wetness of sample was 318 wt.%. Then the product was dried at 40°C for 30 minutes.

The 3.37 weight parts of the modified nonwoven sample containing 2.7 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 15.6 N/50 mm, elongation of 3% as well as LOI of 18.1%.

At the same time the standard acrylic bonding agent of RN-1809 was used by this same method. The acrylic resin content in a nonwoven sample was 33 wt.% on a sample weight. The sample was characterized by tensile strength of 37.2 N/50 mm, elongation of 31.2% and LOI of 18.1%.

EXAMPLE 11

3.28 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 10 was introduced to spraying using 0.5 wt.% water

The 3.60 weight parts of the modified nonwoven sample containing 4.3 wt.% of microcrystalline chitosan was obtained.

The sample was characterized by tensile strength of 36.8 N/50 mm, elongation of 2%, LOI of 18.3% and as wet, after soaking in water for 10 min, the sample was characterized by tensile strength of 11.5 N/50 mm and elongation of 2%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 9

3.45 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 7 was introduced to spraying using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 1. The wetness of sample was 668 wt.%. Then the product was dried at 40°C for 30 minutes.

The 360 weight parts of the modified nonwoven sample containing 4.3 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 37,3 N/50 mm and elongation of 2%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

dispersion of microcrystalline chitosan characterized by properties described in Example 1. The wetness of sample was 318 wt.%. Then the product was dried at 105°C for 5 minutes.

The 3.37 weight parts of the modified nonwoven sample containing 2.7 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 16.8 N/50 mm, elongation of 3%, LOI of 18.1% and as wet, after soaking in water for 10 min, the sample was characterized by tensile strength of 3.2 N/50 mm and elongation of 6%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 12

5.62 weight parts of the nonwoven made of polyester fibres characterized by specific weight of 41 g/m² and tensile strength for the standard conditions of 57 N/50 mm and elongation in standard conditions of 25% as well as LOI of 17.0% was introduced to spraying using 0.5 wt.% dispersion of microcrystalline chitosan in water of pH 7.6 prepared from the microcrystalline chitosan gel-like raw material containing 2.25 wt.% of polymer characterized by deacetylation degree of 62.5%, average molecular weight of 4.28×10^5 and water retention value WRVg of 770%. The wetness of sample was 274 wt.%. Then the product was dried at 40°C for 30 minutes.

The 5.77 weight parts of the modified nonwoven sample containing 2.7 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 15.6 N/50 mm, elongation of 3% as well as LOI of 17.9%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 13

5.62 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 12 was introduced to spraying using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 1. The wetness of sample was 274 wt.%. Then the product was dried at 105°C for 5 minutes.

The 5.77 weight parts of the modified nonwoven sample containing 2.7 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 16.8 N/50 mm, elongation of 2% and LOI of 17,9%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 14

3.2 weight parts of the nonwoven made of polyester fibres characterized by specific weight of 26 g/m² and tensile strength in the standard conditions of 24.3 N/50 mm as well as in wet conditions of 0 N/50 mm and elongation in standard conditions of 1.0% as well as LOI of 17% was introduced to spraying using 0.5 wt.% dispersion of microcrystalline chitosan in water of pH 7.6 prepared from the microcrystalline chitosan gel-like raw material containing 2.25 wt.% of polymer characterized by deacetylation degree of 64%, average molecular weight of 2.45×10^5 and water retention value WRVg of 630%. The wetness of sample was 110 wt.%. Then the product was dried at 105°C for 5 minutes.

The 3.21 weight parts of the modified nonwoven sample containing 0.3 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 26.5 N/50 mm, elongation of 2% as well as LOI of 16.6%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 15

3.36 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 14 was introduced to spraying using 0.5 wt.% water dispersion of microcrystalline chitosan characterized

by properties described in Example 14. The wetness of sample was 205 wt.%. Then the product was dried at 105°C for 5 minutes.

The 3.42 weight parts of the modified nonwoven sample containing 2.1 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 30.1 N/50 mm and elongation of 1.8%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 16

3.17 weight parts of the nonwoven made of the polyester fibres characterized by properties from Example 14 was introduced to spraying using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 7. Then the product was dried at 105°C for 5 minutes.

The 3.42 weight parts of the modified nonwoven sample containing 7.9 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 44.8 N/50 mm, elongation of 3% and LOI of 17,8%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 17

3.27 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 14 was introduced to spraying using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 14. The wettness of sample was 304 wt.%. Then the product was dried at 105°C for 5 minutes.

The 3.34 weight parts of the modified nonwoven sample containing 2.1 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 30.0 N/50 mm and elongation of 2%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 18

3.29 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 1 was introduced to foulardizing using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 7. Then the product was dried at 105°C for 5 minutes.

The 3.33 weight parts of the modified nonwoven sample containing 1.2 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 22.5 N/50 mm and elongation of 2%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 19

3.27 weight parts of the nonwoven made of polyester fibres characterized by properties from Example 1 was introduced to foulardizing using 0.5 wt.% water dispersion of microcrystalline chitosan characterized by properties described in Example 4. Then the product was dried at 105°C for 5 minutes.

The 3.55 weight parts of the modified nonwoven sample containing 8.6 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 20.5 N/50 mm and elongation of 2%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 20

3.27 weight parts of the nonwoven made of polyester fibres characterized by specific weight of 26 g/m² and tensile strength in the standard conditions of 24.3 N/50 mm as well as in wet conditions of 0 N/50 mm and elongation in standard conditions of 1.0% as well as LOI of 17% was introduced to foulardizing

using 0.5 wt.% dispersion of microcrystalline chitosan in water of pH 7.6 prepared from the microcrystalline chitosan gel-like raw material containing 2.25 wt.% of polymer characterized by deacetylation degree of 62.5%, average molecular weight of 4.28×10^5 and water retention value WRVg of 770%. To this dispersion was added LiCl so, that the dispersion contained 0.1% by weight calculated on the dry weight content of chitosan. Then the product was dried at 105°C for 5 minutes.

The 3.40 weight parts of the modified nonwoven sample containing 4.0 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 32.8 N/50 mm, elongation of 2% as well as LOI of 17.0%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 21

3.17 weight parts of the nonwoven made of polyester fibres characterized by specific weight of 26 g/m² and tensile strength in the standard conditions of 24.3 N/50 mm as well as in wet conditions of 0 N/50 mm and elongation in standard conditions of 1.0% as well as LOI of 17% was introduced to foulardizing using 0.5 wt.% dispersion of microcrystalline chitosan in water of pH 7.6 prepared from the microcrystalline chitosan gel-like raw material containing 2.25 wt.% of polymer characterized by

deacetylation degree of 62.5%, average molecular weight of 4.28×10^5 and water retention value WRVg of 770%. Then the product was dried at 105°C for 5 minutes.

The 3.28 weight parts of the modified nonwoven sample containing 3.5 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 32.3 N/50 mm, elongation of 2% as well as LOI of 16.8%.

A sample, where the well-known acrylic resin was used as a bonding agent of nonwoven according to this same method was also obtained. The properties of the obtained well-known sample are described in Example 1.

EXAMPLE 22

16.68 weight parts of 100% cotton fabric of 148 g/m² characterized by tensile strengt of 687 N/50 mm, elongation of 15% and LOI of 17.7% with a standard air conditioning was subjected to spraying by the microcrystalline chitosan water dispersion containing 0.51 wt.% of polymer characterized by properties described in Example 1. The wetness of sample was 294.8%. Then a sample was dried at 105°C for 5 minutes.

The 17.37 weight parts of modified cotton fabric was obtained. The sample contained 4.1% of microcrystalline chitosan.

The sample was characterized by tensile strength of 771 N/50 mm, elongation of 20% and LOI of 18.4. The sample was dyeable also by the acid dyes.

EXAMPLE 23

17.75 weight parts of 100% cotton fabric characterized by properties described in Example 22 was impregnated in the foulard by the microcrystalline chitosan water dispersion containing 0.51 wt.% of polymer characterized by properties described in Example 22. The impregnation speed was 2 m/min. Then the sample was dried at 105°C for 5 minutes.

The 18.07 weight parts of modified cotton fabric containing 1.8 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 689 N/50 mm, elongation of 14% and LOI of 17.8%. The sample was dyeable also by the acid dyes.

EXAMPLE 24

18.84 weight parts of the knitwear sample made of cotton fibres characterized by tensile strength of 352 N/50 mm, elongation of 59% and LOI of 18.2% with a standard air conditioning was subjected to spraying by the microcrystalline chitosan water dispersion containing 0.51 wt.% of polymer characterized by properties described in Example 1. The wetnes of sample was 136.6%. Then the sample was dried at 40°C for 30 minutes.

EXAMPLE 27

3.41 weight parts of the leather sample characterized by properties described in Example 26 was sprayed on both sides with the microcrystalline chitosan water dispersion as in Example 21 containing 0.01 wt.% Sandozin NIT as in Example 21. The sample was dried at 40°C until dry.

3.60 weight parts of the modified leather sample containing 5.6 wt.% of the microcrystalline chitosan was obtained. This sample was characterized by tensile strength of 38.0 N/5 mm and elongation of 54%.

The 19.71 weight parts of the modified knitwear sample containing 4.6 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 369 N/50 mm, elongation of 58% and LOI of 18.9%.

EXAMPLE 25

18.92 weight parts of the knitwear sample made of cotton fibres characterized by properties described in Example 24 was impregnated in the foulard by the microcrystalline chitosan water dispersion with properties described in Example 22. The impregnation speed was 2 m/min. Then the sample was dried at 105°C for 5 minutes.

The 19.22 weight part of modified knitwear sample containing 1.6 wt.% of microcrystalline chitosan was obtained. The sample was characterized by tensile strength of 304 N/50 mm, elongation of 55% and LOI of 18.8%.

EXAMPLE 26

3.07 weight parts of the leather sample of the New Zealand Lamb's Suede characterized by tensile strength of 50.9 N/5 mm and elongation of 61% was sprayed on both sides with the microcrystalline chitosan water dispersion according to Example 7. The sample was dried in 40°C until dry.

3.27 weight parts of the modified leather sample containing 6.5 wt.% of the microcrystalline chitosan was obtained. This sample was characterized by tensile strength of 60.7 N/5 mm and elongation of 58%.

Claims:

1. The modified fibrous products, especially fabrics, nonwovens, knitwears, leathers and the like, comprising chitosan after treatment by chitosan as a modifying material, characterized in that the chitosan is microcrystalline chitosan, the product containing microcrystalline chitosan particles bonded to adjacent particles and the structure of the fibrous product mainly by hydrogen bonds.

2. The modified fibrous products as claimed in claim 1, characterized in that the product contains not less than 0.01 wt.% of microcrystalline chitosan, preferably 0.5-10 wt.%.

3. A modified fibrous product as claimed in claim 2, characterized in that the product contains modifying chemical additives up to 10 wt.% on the microcrystalline chitosan weight.

4. The modified fibrous products, especially fabrics, nonwovens, knitwears, leathers, as claimed in claim 1 to 3, characterized in that the microcrystalline chitosan used as a modifying material, such as gel-like dispersion, preferable in water, has especially a water retention value of the gel-like form within a range of 500-2000% and 200-800% in a powder form, average molecular weight within a range 10^4-10^6, deacetylation degree not less than 30%, preferable 40-80% and preferably particles dimension within a range of 0.01 to 100 µm.

5. The modified fibrous products as claimed in claims 1 to 4, c h a r a c t e r i z e d in that the modifying chemical additives are inorganic salts as well as organic compounds as lithium chloride or surfactants.

6. A method of manufacture of the modified fibrous products, c h a r a c t e r i z e d in that the microcrystalline chitosan gel-like dispersion, especially in water is brought in contact with the fibrous products, especially fabrics, nonwovens, knitwears, leathers and the like, preferably by dipping, immersing, spraying or foularding, whereafter the products are dried.

7. A method as claimed in claim 6, c h a r a c t e r i z e d in that the microcrystalline gel-like dispersion used contains not less than 0.001 wt.% of the polymer on a dry weight and has a pH not less than 7.00, especially in the range 7.00-10.00.

8. A method as claimed in claim 6 or 7, c h a r a c t e r i z e d in that the addition of the modifying chemical additives is carried out directly to the microcrystalline chitosan before or during distribution of microcrystalline particles into a liquid medium or to the liquid medium as well as during the modification of fibrous products, preferably by spraying through nozzles or similar.

FIG 1a

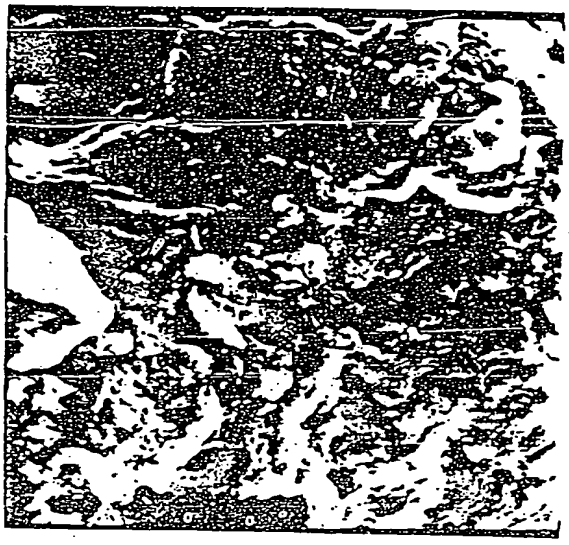

FIG 1b

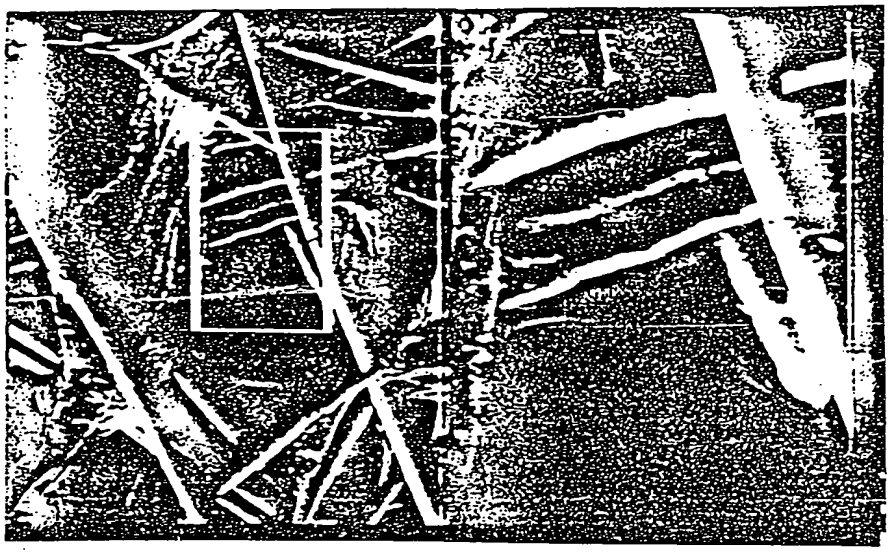

FIG 2a

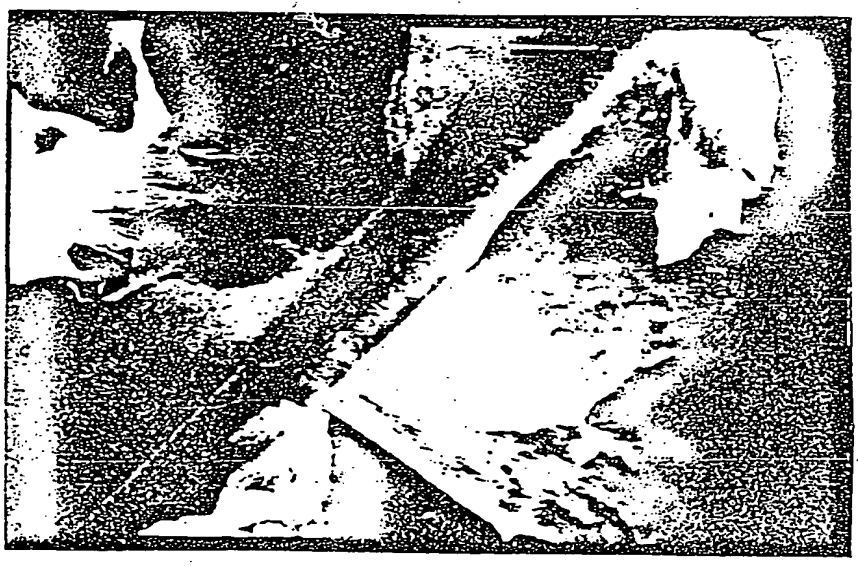

FIG 2b

FIG 2c

FIG 2d

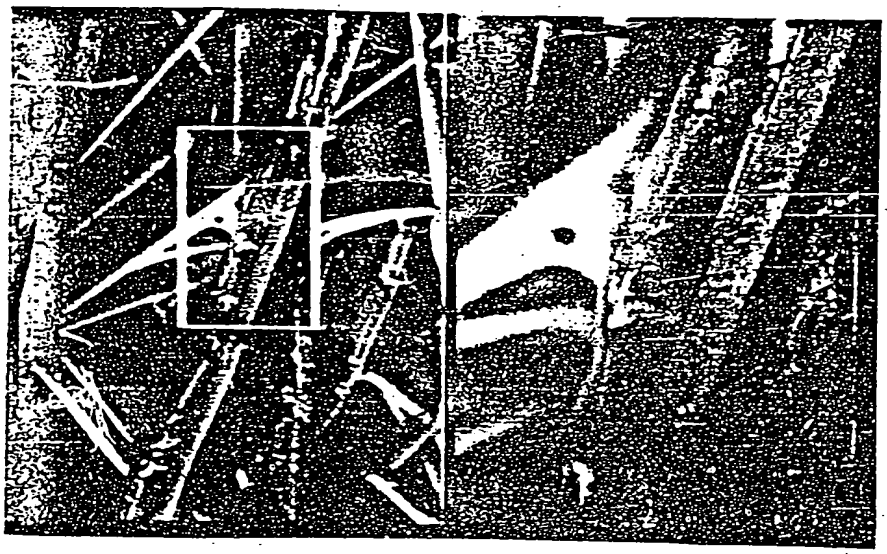

FIG 2e

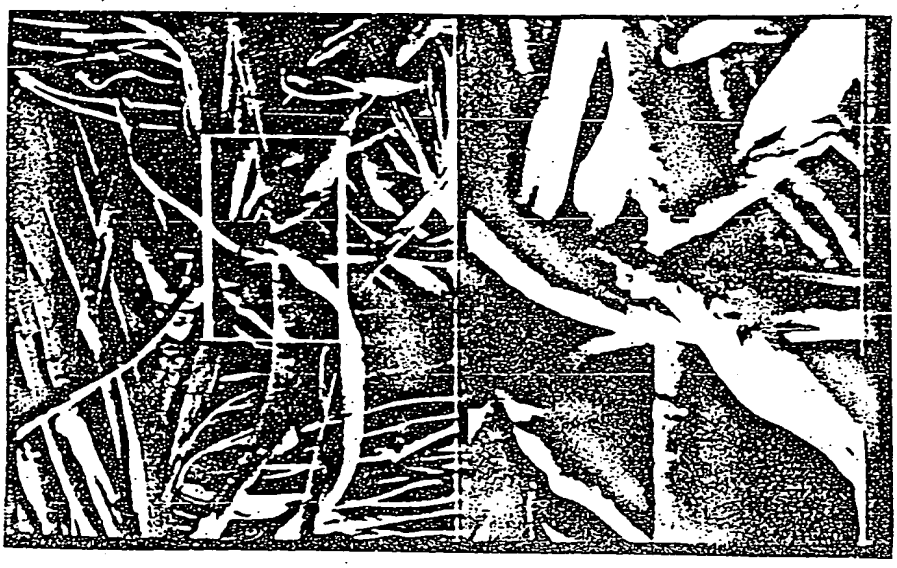

FIG 3a

FIG 3b

FIG 3c

INTERNATIONAL SEARCH REPORT

International Application No PCT/FI87/00104

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC 4

D 06 M 15/03, C 14 C 9/00

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC 4	C 08 B 37/08; C 14 C 9/00; D 06 M 15/03; D 06 P 1/48; D 21 M 3/20
US Cl	8:115.58, 115.61, 181; 106:162; 162:175

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [10]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	PL, B2, 133 745 (POLITECHNIKA LODZKA, LODZ) 30 June 1986	1-8

[10] Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
1987-11-17	1987 -11- 23
International Searching Authority	**Signature of Authorized Officer**
Swedish Patent Office	Ingrid Falk

LH

FIG 4a

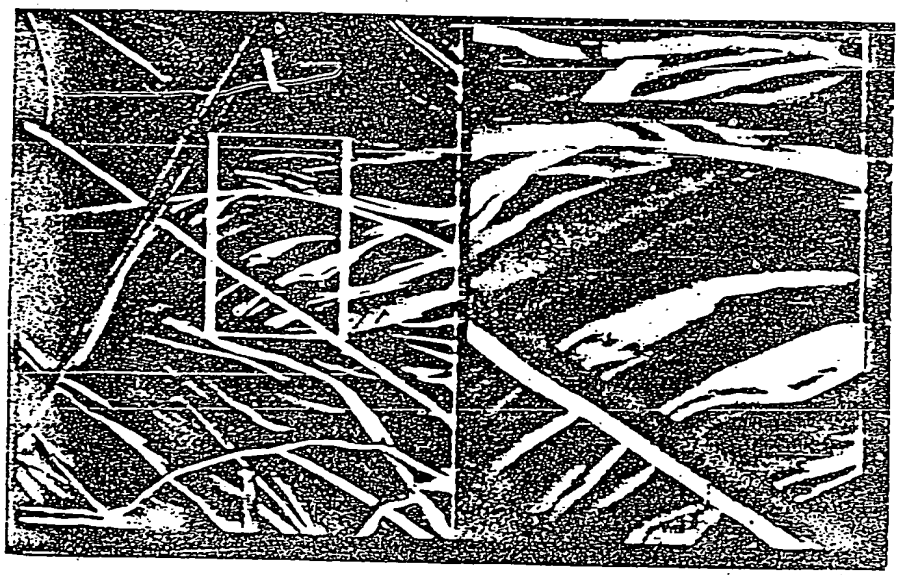

FIG 4b